

# PATENT SPECIFICATION

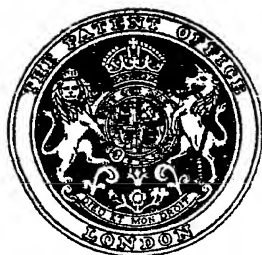
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## COMPLETE SPECIFICATION

### Recovery of Polycarboxylic Acid Anhydrides

We, CHEMPATENTS, INC., of 2, Park Avenue, New York, New York, United States of America, a corporation organised under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the recovery of the anhydrides of polycarboxylic acids, and has particular reference to a method for the recovery and purification of phthalic anhydride and maleic anhydride from gaseous mixtures containing the anhydrides in the vapour phase.

The anhydrides of maleic and phthalic acid are obtained by the oxidation of benzene and naphthalene respectively, in the presence of a suitable oxidation catalyst. The benzene or naphthalene starting material is mixed with an oxidizing gas such as air, and the mixture brought into contact with the selected oxidation catalyst. The resulting gaseous reaction mixture will contain anhydride in the vapour phase, water vapour formed as a by-product of the oxidation reaction, nitrogen, carbon monoxide, and carbon dioxide, as well as residual by-products, and an excess of oxygen.

There are several known procedures for the manufacture of phthalic anhydride from organic compounds, such as naphthalene, by oxidation. One such process embodies the catalytic oxidation of naphthalene or ortho-xylene, using a fixed bed type catalytic system embodying tubular converters packed with catalyst. The same process is employed in the manufacture of maleic anhydride from benzene. Fluid catalyst systems wherein the heat of reaction is removed, for example, by continuous circulation of the catalyst through a cooling zone outside the catalytic reactors, are more advantageously employed, for this type of system permits of substantial reduction in equipment cost due to simplification and marked increase in capacity of standard equipment. In spite of the basic similarity of the procedures employed in the manufacture of phthalic and maleic anhydrides, at the present

time it is necessary to provide separate systems for the production of these materials, embodying considerable expensive duplication of equipment and waste of space, due to the procedural difficulties involved in the recoveries of each of the anhydrides.

Several different methods for the recovery of the anhydrides from the reactor gases, are currently in use. For example, in the case of maleic anhydride, the compound may be withdrawn from the gaseous reaction mixture by scrubbing with water to produce maleic acid, which is then dehydrated in a subsequent procedure to obtain the anhydride. The use of solvents for the direct absorption of the anhydride from the gaseous reaction mixture has also been suggested, but until recently the solvent type recovery process has had the disadvantage of requiring separate systems for the recovery of maleic and phthalic anhydrides, involving excessive overhead expense of purchase, installation and operation of equipment, as well as excessive operating space. Moreover, the solvents employed have involved a considerable hazard of accidental explosion, due to the characteristic presence of relatively large amounts of oxygen in the gaseous reaction mixture emerging from the reactors. Solvents having relatively low boiling points and high vapour pressures, cannot be considered safe to use, or practical from the standpoint of solvent loss, end product contamination through thermal decomposition, and in other respects.

U.S. Patent Specification No. 2,574,644 describes a system for the recovery of polycarboxylic acid anhydrides, which system is adaptable for the recovery of a specific anhydride simply by changing operating conditions of the system. That system was based on the discovery that dibutyl phthalate is selectively absorbent towards maleic and phthalic anhydrides in the vapour state under certain operating conditions, and that this solvent selectivity may be exploited simply by modifying the operating conditions attending the use of the anhydride recovery system within certain critical limits, whereby the same system



may be employed to recover both maleic and phthalic anhydrides.

Phthalic anhydride is substantially insoluble in dibutyl phthalate at room temperature, but upon heating to approximately 70° C. to 120° C. the solubility of phthalic anhydride in dibutyl phthalate increases markedly to such an extent that solvent solutions containing from 10% to 20% of phthalic anhydride as the solute, with low vapour pressure of solute over the solutions, can readily be obtained. On the other hand, maleic anhydride is much more soluble in dibutyl phthalate at lower temperatures (approximating the range of 10° C. to 70° C.), than phthalic anhydride. Higher temperatures result in increased loss of maleic anhydride by volatilization. Accordingly, therefore, the U.S. Specification describes an anhydride recovery and purification system that may be operated within the one temperature range for the recovery of phthalic anhydride and within the second range for the recovery of maleic anhydride, without further modification of the system, the system being designed initially to accommodate the more severe operating conditions incident to the recovery of phthalic anhydride, whereby the recovery of maleic anhydride may be accomplished merely by modifying the process to embody the less severe operating conditions arising from its greater solubility in the solvent at lower temperatures, and its lower melting and boiling points. The single anhydride recovery and purification system may be employed with gases emerging from the catalytic reactors, whether the gases contain maleic or phthalic anhydride or both, combining in one recovery plant procedure normally embodying two different recovery systems requiring separate installation. The fluid catalyst process increases the rate of reaction and reactor unit output ratio, in comparison with fixed bed type catalyst systems, and has the further advantage of substantially reducing the oxygen starting material ratio required, as against that required for a fixed bed operation, obtaining a larger concentration of anhydride in the reactor gases. This feature permits the use of smaller reactor and recovery or absorption systems and concentration of the anhydrides in the gaseous reaction mixtures to a more economical and readily recoverable level.

The method as applied to the recovery of maleic anhydride has the further advantage of eliminating the formation of fumaric and maleic acids (which are obtained by present commercial methods using water scrubbing) as by-products. Fumaric and maleic acids have a relatively minor industrial application, compared with maleic anhydride.

This recovery and purification system may be advantageously employed with either the fixed bed or fluid catalyst type of reaction process for the production of anhydride. It may likewise be used to recover maleic an-

hydride and phthalic anhydride from a gaseous mixture containing both, by first passing the mixture over dibutyl phthalate to absorb phthalic anhydride at an appropriate temperature, and then passing the mixture from which phthalic anhydride has been removed over dibutyl phthalate at an appropriate lower temperature, the phthalic anhydride and the maleic anhydride being subsequently stripped from the respective solutions.

The present invention is concerned with the separation of maleic and phthalic anhydrides from gaseous mixtures in which both are present, using dibutyl phthalate as a selective solvent.

According to the present invention, a gaseous mixture containing maleic and phthalic anhydrides is passed in contact with dibutyl phthalate solvent for simultaneous absorption of both anhydrides, which is followed by stripping the absorbed anhydrides from the solution.

The absorption may be effected under conditions such that the resulting solution contains both maleic and phthalic anhydrides, the stripping then producing a mixture of both anhydrides, which may then be separated, e.g. by fractionation.

Again, the absorption may be accompanied by simultaneous stripping of the maleic anhydride, leaving phthalic anhydride to be stripped from a solvent substantially free from maleic anhydride. Thus, stripping of maleic anhydride may be effected by a counter-current of inert gas (e.g. nitrogen, or reaction gas from which the anhydrides have been stripped), and the resultant stream containing maleic anhydride may be treated for recovery of the latter if the amount present justifies such treatment.

The invention will now be described in greater detail with reference to the accompanying drawings, in which

Figure 1 is a flow sheet of a process suitable for both the recovery of maleic or phthalic anhydride from gaseous mixtures containing one only of these anhydrides, and also, in accordance with the invention, the recovery of the anhydrides from gaseous mixtures containing both of them; and

Figure 2 is a flow sheet of another process according to the invention for the recovery of the anhydrides from gaseous mixtures containing both anhydrides.

Referring to Figure 1, dilute feed gas is fed into an absorber tower 10, which may contain baffles, Raschig rings, or the like means to ensure contact between the gas and the solvent fed into the top of the tower 10 through a spray or other dispersing device. The enriched solvent is withdrawn from the bottom of the tower 10, heated by passage through a heat exchanger 11, and is introduced into the base of a plate (bubble-cap or like) rectifier or stripper 12, which is heated by a calandria or



the like 13. Subatmospheric pressure is maintained in the rectifier 12 by a steam jet ejector 14 or a vacuum pump. Distillate from the top of the rectifier 12 is condensed in a condenser 15, a portion being returned as reflux, and the remainder being withdrawn through a conduit 16, for further refining of the product if necessary.

The stripped solvent comprising the bottom of the rectifier 12 is withdrawn from the base and passed to a plate stripper 17, operating under generally similar conditions to the rectifier 12, where remaining traces of anhydride are removed and returned to an appropriate point in the rectifier 12 as at 18 for redistillation. A reflux condenser 19 and a calandria 20

are provided with the stripper 17.

Stripped solvent from the base of the stripper 17 contains very little anhydride, and this is returned to the absorber 10 through the heat exchanger 11, when a portion of the heat is transferred to the enriched solvent passing from the absorber 10 to the rectifier 12. The stripped solvent is passed through a cooler 21 to bring it to a suitable temperature for re-introduction to the top of the absorber 10.

Before reference is made to the operating conditions necessary when both anhydrides are present in the feed gas, the following details are given of the conditions when only one anhydride is present:—

| Typical feed: Anhydride |  | Phthalic anhydride<br>1.9%   | Maleic anhydride<br>1.0%                                   |
|-------------------------|--|--|--|
| 35                      | Oxygen                                       | 8.4  | 8.6  |
|                         | Carbon dioxide                               | 6.9  | 8.0  |
|                         | Water  | 5.0  | 5.0  |
|                         | Nitrogen                                     | 77.8   | 77.4   |
|                         |  | <u>100.0</u>   | <u>100.0</u>   |
| 40                      | Gas feed temperature to absorber 10          | 70°C. to 125°C., preferably 100°C. (or up to 170°C. with cooler solvent) | 40°C. to 70°C. preferably 60°C.                            |
| 45                      | Solvent feed temperature                     | 70°C. to 125°C. preferably 100°C.  | 40°C. to 70°C. preferably 60°C.                            |
|                         | Enriched solvent temperature to rectifier 12 | 150°C. to 250°C. preferably 205°C.                                       | 75°C. to 175°C. preferably 170°C.                          |
|                         | Base temperature of rectifier 12             | 220°C. (max. 230°C.)   | 115°C. (as reduced by reflux)                              |
| 50                      | Top temperature of rectifier 12              | —  | 75°C.  |
|                         | Pressure of rectifier 12                     | 10 mm. to 150 mm. Hg.  | 10 mm. to 150 mm. Hg.                                      |
|                         | Bottom pressure                              | preferably 55 mm.  | preferably 45 mm.  |
| 55                      | Top pressure                                 | 5 mm. 50 mm. preferably 33 mm.   | preferably 23 mm.  |
|                         | Temperature of stripper 17                   | 150°C. to 245°C. preferably 220°C.                                       | 79°C. to 250° C. preferably 220°C. at bottom, 79°C. at top |
|                         | Pressure in stripper 17                      | 10 mm. to 55 mm.   | 10 mm. to 130 mm.  |
| 60                      | Bottom, preferably                           | 55 mm.   | 25 mm. to 30 mm.   |
|                         | Top, preferably                              | 23 mm.   | 10 mm. to 15 mm.   |



The separation of either the maleic or phthalic anhydride from the dibutyl phthalate solvent is accomplished by stripping under preferred conditions of temperature and pressure, whereby a maximum recovery of the particular anhydride is effected, with a minimum loss of anhydride or solvent to waste. Due to the low vapour pressure of dibutyl phthalate, virtually none of the solvent is lost through evaporation during the stripping operation. Also, the thermal resistance of this solvent is such that it withstands the temperature necessary for the stripping operation with very little loss through thermal decomposition. It has been found that dibutyl phthalate is thermally stable at a temperature approximating even 250° C. in the presence of metals. It is this unusual and unexpected stability of this solvent which renders this recovery system operative and feasible from a commercial standpoint.

Further in this connection, it will be noted that the low rate of thermal decomposition of dibutyl phthalate experienced under the more extreme operating conditions of the method, for example as employed in the separation of phthalic anhydride, is of no material consequence, for dibutyl phthalate breaks down into phthalic anhydride, butyl alcohol, and butylene. As the butyl alcohol and butylene constituents are volatile, these possible contaminants are evacuated by the low pressure system employed in the stripping operation. The anhydride, of course, adds to the amount of end product recovered. Consequently, no impurities or contaminants are introduced into the system, during the separation of phthalic anhydride from the dibutyl phthalate solvent. As lower temperatures are employed in the separation of maleic anhydride, thermal decomposition of dibutyl phthalate solvent is less of a problem, and the minor amount of phthalic anhydride formed is readily separated from the maleic anhydride, and used to augment the phthalic anhydride produced at other times in the same plant.

The highly inert character of the dibutyl phthalate solvent also minimizes the significance of the presence of oxygen in the reaction mixture. The solvent has such a high boiling point that it will not react therewith under the operating conditions set forth, thereby eliminating the explosion hazard.

The system of Figure 1 is directly applicable for the utilisation, according to one method of carrying out the invention, of the ability of the dibutyl phthalate to absorb both maleic and phthalic anhydrides by absorbing the two anhydrides in the absorber 10 and then directing the anhydride-rich solvent through the heat exchanger 11 into the rectifier 12. Rectifier 12 is operated under conditions to take both maleic and phthalic anhydrides off the top of the rectifier as an overhead product. The bottoms from the rectifier 12 are delivered to

the stripper 17 which removes any anhydride which may remain in the solvent as an overhead product. The anhydride is returned through line 18 to the rectifier and the stripped solvent is returned through heat exchanger 11 and cooler 21 to the absorber 10.

When operating according to the procedure described in the preceding paragraph, the pressure at the top of the rectifier 12 is controlled between about 10 and 33 mm. of mercury absolute, and the temperature is maintained between 40° C. and 175° C., preferably between 75° C. and 172° C. The pressure at the bottom of the rectifier 12 is maintained at about 45 to 130 mm. mercury absolute and the temperature at 115° C. to 250° C.

The stripper 17 which removes the traces of maleic and phthalic anhydrides from the solvent is preferably operated at an absolute pressure of 10 to 25 mm. of mercury at the top of the stripper and a temperature ranging from 80° C. to 200° C. in that region. It will be appreciated that the temperature at the top of the rectifier and stripper will depend upon the relative concentrations of maleic and phthalic anhydrides in the rich solvent delivered to the rectifier. The temperature at the bottom of stripper 17 is maintained at about 220° C. to 250° C., and the absolute pressure is about 25 to 150 mm. of mercury, under which conditions effective stripping of the solvent is obtained.

The mixture of phthalic and maleic anhydrides taken from the top of the tower 12 is condensed in the cooler 15, and the two anhydrides may then be separated by conventional fractionation procedures.

Another method of carrying out the invention involves the use of the system shown in Figure 2. Reaction gases are delivered through a line 25 into an absorber-stripper 26 at a temperature preferably in the neighbourhood of about 170° C. to 200° C. Dibutyl phthalate is introduced into the top of the tower through line 27 and absorbs phthalic anhydride in the feed gases as it descends through the tower. As the phthalic anhydride-rich solvent passes downwardly from the feed point, it passes counter-currently to inert gases introduced into the bottom of the tower through line 28. The inert gases strip maleic anhydride from the solvent to discharge a substantially maleic anhydride-free solution of phthalic anhydride in the dibutyl phthalate from tower 26. The inert gas may be nitrogen or the reaction gases from which maleic and phthalic anhydrides have been stripped. For efficient stripping of the maleic anhydride from the solvent, it is preferred that the absorber-stripper 26 be operated at an absolute pressure of approximately 100 mm. of mercury, and a temperature of 230° C.

The phthalic anhydride-rich solvent is introduced into a stripper 29 maintained at an



absolute pressure of 10 to 55 mm. of mercury by conventional ejector means. A calandria 30 at the base of the tower maintains the dibutyl phthalate at a temperature of about 230° C. which effectively strips the phthalic anhydride from the solvent. Phthalic anhydride-free solvent is withdrawn from the bottom of the stripper and cooled in heat exchanger 31 before returning to the top of the absorber-stripper 26 through line 27. Phthalic anhydride is taken from the top of stripper 29, condensed in condenser 32, and recovered in any suitable manner such as by flaking.

Instead of returning direct to the heat exchanger 31, the bottoms from the stripper 29 may be fed to a further stripper corresponding to the stripper 17 of Figure 1.

The maleic anhydride discharged from the top of absorber-stripper 26 may be discarded if present in very low concentrations. If present in amounts justifying the necessary capital investment, the maleic anhydride may be recovered from the inert gas in a second recovery unit, for example a unit as in Figure 1.

Single and double stripping operations have been described; but more than two stripping steps may be used, if desired.

The feed gases may be cooled prior to absorption if the anhydride concentration is sufficiently high, to liquefy some of the anhydride, which may then be separated from the gases.

What we claim is:—

1. A process for the recovery of anhydrides from a gaseous mixture containing both maleic anhydride and phthalic anhydride, comprising passing the mixture in contact with dibutyl phthalate solvent at at least 40° C. for simultaneous absorption of both anhydrides, and stripping the absorbed anhydrides from the solution.

2. A process for the recovery of maleic anhydride and phthalic anhydride from a gaseous mixture containing both anhydrides, comprising passing the mixture in contact with dibutyl phthalate solvent at at least 40° C. for simultaneous absorption of both anhydrides, and stripping a mixture of the absorbed anhydrides from the solution.

3. A process as in Claim 2, wherein the absorption is effected in the temperature range of 40° C. to 175° C.

4. A process as in Claim 2 or Claim 3, wherein the stripping is effected in a stripper having bottom temperature and pressure in the ranges 115° C. to 250° C. and 45 mm. to 130 mm. mercury, and top temperature and pressure in the ranges 75° C. to 172° C. and

10 mm. to 33 mm. mercury.

5. A process as in Claim 4, wherein the bottoms from the stripper are subjected to further stripping with bottom temperature and pressure in the ranges 220° C. to 250° C. and 25 mm. to 150 mm. mercury, and top temperature and pressure in the ranges 80° C. to 200° C. and 10 mm. to 25 mm. mercury, and the top product of the second stripping is returned to the first stripper.

6. A process for the recovery of anhydrides from a gaseous mixture containing both maleic anhydride and phthalic anhydride, comprising passing the mixture in contact with dibutyl phthalate solvent at at least 40° C. for simultaneous absorption of both anhydrides, stripping the maleic anhydride from the dibutyl phthalate, and subsequently stripping phthalic anhydride from the dibutyl phthalate substantially free from maleic anhydride.

7. A process for the recovery of anhydrides from a gaseous mixture containing both maleic anhydride and phthalic anhydride, comprising passing the mixture in contact with dibutyl phthalate solvent at at least 40° C. for simultaneous absorption of both anhydrides, simultaneously passing an inert gas through the dibutyl phthalate to strip maleic anhydride therefrom, and subsequently stripping phthalic anhydride from the dibutyl phthalate substantially free from maleic anhydride.

8. A process as in Claim 7, wherein the absorption is effected with the gaseous mixture in the temperature range 170° C. to 200° C., the temperature of the dibutyl phthalate is approximately 230° C., and the pressure is approximately 100 mm. mercury.

9. Process as in Claim 7 or Claim 8, wherein the stripping of the phthalic anhydride is effected in a stripper with a bottom temperature of approximately 230° C., the pressure in the stripper being in the range 10 mm. to 55 mm. mercury.

10. Process as in any of Claims 7 to 9, wherein maleic anhydride is recovered from the inert gas by absorption in dibutyl phthalate and subsequent stripping.

11. Process as in any of Claims 1 to 10, wherein the feed gas is cooled for condensation and separation of some anhydride prior to absorption.

12. Processes for the simultaneous recovery of mixed maleic and phthalic anhydrides and their subsequent separation substantially as hereinbefore described.

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